AD-A157 235 ADHESIVE BONDING OF NEOPRENE TO METAL IN SONAR DEVICES 1/1
(U) CINCINNATI UNIV OH DEPT OF MATERIALS SCIENCE AND
METALLURGICAL ENGINEERING F J BOERIO 01 JUL 85
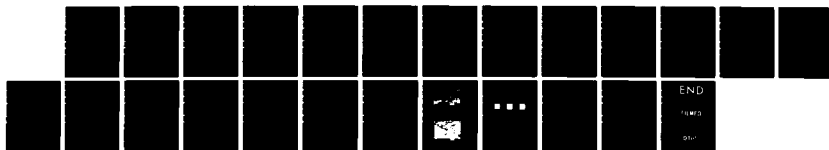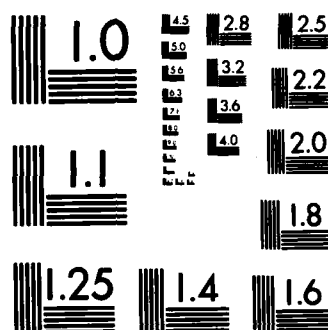UNCLASSIFIED N00014-84-K-0398 F/G 11/1 NL

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Adhesive Bonding of Neoprene to Metal
in Sonar Devices

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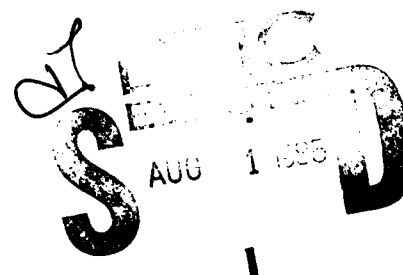University of Cincinnati
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I. INTRODUCTION

The front window on sonar devices is usually prepared by curing a slab of neoprene rubber in contact with a steel shroud and an aluminum head mass. A commercial, proprietary adhesive system consisting of a metal primer and a rubber adhesive is used to bond the window to the shroud and head mass. From time to time large numbers of failures of these bonds have occurred, resulting in the failure of numerous transducers. As a result, there is a need to understand the failure mechanisms of rubber to metal bonds and to develop a new adhesive system with known composition for obtaining strong, durable bonds between neoprene and metals such as aluminum and steel.

Bonding rubbers to metals has always been a difficult process. Most rubbers show very little <u>dry</u> adhesion when cured in contact with the oxidized surfaces of metals. Moreover, it has been stated that it is virtually impossible to obtain a <u>water resistant</u> bond between a rubber and a hydrophilic mineral surface (1). As a result, it is usually necessary to pretreat the substrate surface in some way when bonding rubbers to metals.

One procedure for obtaining strong, durable bonds between rubbers and metals is to use an organic interlayer such as a chlorinated rubber (2). An adhesive based on allylically brominated poly-2,3-dichloro-1,4-butadiene containing 10-27% bromine was patented (3) and the patent was assigned to Lord Corporation. It seems likely that chlorinated rubbers and their halogenated derivatives are important components of Chemlok 205 primer and Chemlok 220 adhesive supplied by Lord Corporation for bonding rubbers to metals.

It is also possible to obtain strong, durable bonds between rubbers and mineral substrates using silane "coupling agents." Most useful silanes

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have the general structure:

$$R—Si—R'_3$$
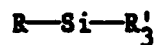
where R is an organofunctional group usually chosen for compatibility with a particular polymer and R' is a functional group that is easily hydrolyzed to form a silanol group. The reactions between silane coupling agents and mineral surfaces can vary significantly depending on the functional group R and the mineral. As a result, the mechanisms by which silanes function as coupling agents are not completely understood. However, one model (4) considers that silanes function by forming stable bonds between mineral substrates and polymers (see Figure 1). When an inorganic substrate is treated with an aqueous solution of a coupling agent, the coupling agent molecules are adsorbed through the silanol groups. During drying, the silanol molecules may polymerize to form siloxane polymers and may also react with surface hydroxyl groups to form primary bonds with the substrate. The functional group R may then react with an adhesive applied to the pretreated substrate (4).

The use of silanes as primers for bonding rubbers to mineral surfaces has been demonstrated. In one case (5), only weak bonds were obtained when polybutadiene was cured against cleaned glass slides. However, when the same rubber was cured against slides that had been primed with thin films of vinyltriethoxysilane, very strong bonds were obtained (5). Similarly, γ-methacryloxypropyltrimethoxysilane (γ-MPS) has been used to obtain water-resistant bonds between ethylene-vinyl acetate elastomers and metals such as steel and aluminum (6).

II. OBJECTIVES

This research has two primary objectives. The first is to develop a new adhesive system based on silane coupling agents for obtaining strong, durable bonds between neoprene and metals such as steel and aluminum in sonar devices. The new adhesive system should provide more reliable bonds between neoprene and metals than commercial, proprietary adhesive systems and, unlike commercial adhesives, should have known composition. The second primary objective is to determine the failure mechanism for rubber/metal adhesive bonds exposed to aggressive environments such as seawater for long periods of time. An additional objective is to characterize a commercial adhesive system such as the Chemlok 205/220 system.

III. PROGRESS

Characterization of Commercial Adhesive Systems

The commercially available adhesive system consisting of Chemlok 205 primer and Chemlok 220 adhesive was characterized using infrared spectroscopy, x-ray diffraction, and energy-dispersive x-ray analysis (EDAX). It was felt that the results obtained would be useful in developing improved, non-proprietary adhesive systems for bonding rubbery polymers such as neoprene to metals such as steel and aluminum.

Chemlok 205 consists of organic polymers dissolved in solvents and with inorganic solids dispersed in the solution. The dispersed solids were separated from the polymer solution by centrifugation and were thoroughly rinsed with solvents such as methylethylketone (MEK) to remove residual polymer. Thin films of the polymer were prepared for analysis by casting the polymer solution onto a teflon plate and allowing the solvent to evaporate.

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The infrared spectrum of the polymer separated from Chemlok 205 is shown in Figure 2. The spectrum is characterized by a strong band near 1235 cm^{-1} and by medium intensity bands near 1695, 1613, 1600, 1513, 1481, 1449, 1387, 1366, 1152, 1117, 1010, 888, 826, 781, and 758 cm^{-1}. Comparison of the observed spectrum with published reference spectra enabled the main component of the polymer to be identified as a phenol/formaldehyde polymer of the type known as resoles. Results obtained using EDAX showed that Chemlok 205 contains a significant amount of chlorine. As a result, it was concluded that Chemlok 205 may also contain a chlorinated rubber. However, the composition of that rubber is not known for certain at this time.

The infrared spectrum of the dispersed solids separated from Chemlok 205 was characterized by a strong band near 675 cm^{-1} and by a weaker band near 1110 cm^{-1} (see Figure 3). When the observed spectrum was compared with reference spectra, the band near 675 cm^{-1} was assigned to the rutile form of TiO_2 and the band near 1110 cm^{-1} was assigned to an aluminum silicate.

The x-ray scattering spectrum obtained from the inorganic solids separated from Chemlok 205 is shown in Figure 4. Reference x-ray spectra of rutile TiO_2 and ZnO are shown in Figures 5 and 6, respectively. It is evident that the strong bands in the spectrum of the Chemlok 205 solids can be assigned to the rutile form of TiO_2. Most of the weaker bands can be assigned to ZnO. A few of the weak bands can be assigned to an aluminum silicate.

These results indicate that Chemlok 205 primer consists of a phenol/formaldehyde polymer, probably blended with a chlorinated rubber. The primer also contains dispersed solids such as carbon black, rutile

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TiO_2, ZnO, and an aluminum silicate. Chemlok 205 may contain small amounts of other compounds such as silane coupling agents. However, it is felt that the major constituents of Chemlok 205 have been identified.

Chemlok 220 adhesive also consists of organic polymers dissolved in solvents and with carbon black dispersed in the solution. However, in this case it was not possible to separate the dispersed carbon black from the solution. Instead, a thin film was prepared by diluting a small amount of Chemlok 220 with MEK, casting the dispersion onto a teflon plate, and allowing the solvent to evaporate. The infrared spectrum obtained from the film was characterized by strong bands near 1450, 1280, and 720 cm^{-1} and by weaker bands near 1600, 1510, 1390, 1090, 1025, and 925 cm^{-1} (see Figure 7A). Comparison of the observed spectrum with published reference spectra indicated that Chemlok 220 was mainly composed of a chlorinated rubber such as a chlorinated styrene/butadiene or styrene/isoprene copolymer. The spectrum of one such chlorinated rubber, Parlon S-10, is shown for comparison in Figure 7B. It is evident that the band positions are very similar for Chemlok 220 and Parlon S-10.

We have previously found a small amount of bromine in Chemlok 220 using EDAX. As a result, it has been concluded that Chemlok 220 consists mostly of carbon black and a lightly brominated chlorinated rubber similar to Parlon S-10.

Failure Mechanisms of Rubber/Metal Bonds

Another objective of this research is to determine the failure mechanism of rubber to metal bonds by using x-ray photoelectron spectroscopy (XPS) to examine the failure surfaces of bonds after exposure to aggressive environments for long times. The failure of such bonds can occur in one of four phases (rubber, adhesive, primer, or oxide) or near

one of the three interfaces. In order to interpret the XPS spectra obtained from failure surfaces, it will be essential to have available appropriate XPS reference spectra. Accordingly, we have obtained such spectra for Chemlok 205 primer, Chemlok 220 adhesive, and neoprene (see Figures 8, 9, and 10).

Intense bands were observed near 530, 285, and 199 eV in the spectra obtained from Chemlok 205 and assigned to O(1s), C(1s), and Cl(2p) electrons, respectively. Weak bands characteristic of Zn(2p) and Ti(2p) electrons were observed near 1022 and 459 eV, respectively. These results are consistent with the composition of Chemlok 205 as described above.

Intense bands characteristic of C(1s) and Cl(2p) electrons were also observed near 285 and 199 eV in XPS spectra of Chemlok 220. Medium intensity bands characteristic of O(1s) and Cl(2s) electrons were observed near 530 and 270 eV. A weak band was observed near 70 eV and assigned to Br(3d) electrons. These results are also consistent with the composition of Chemlok 220 as described above. However, the oxygen detected in the XPS spectrum may indicate some oxidation of the adhesive or, perhaps, an additive that was not detected by other analytical techniques used to determine the composition of Chemlok 220.

The XPS spectrum of neoprene rubber was dominated by a strong band near 285 eV that was, as usual, assigned to C(1s) electrons. A pair of strong bands was observed near 144 and 139 eV and assigned to Pb(4f) electrons from the red lead curing agent. The medium intensity band near 530 eV was also attributed mostly to the O(1s) electrons from the curing agent. Two weak bands were observed near 415 and 435 eV and assigned to the Pb(4d) electrons of the curing agent.

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Pretreatment of Steel Surface for Adhesive Bonding

We have considered two different pretreatment processes for steel surfaces, a commercial, proprietary alkaline cleaner (Parker 348) and an acid etching solution that was recently described by Trawinski (7). In the first case, steel coupons were immersed in a 6% solution of Parker 348 in deionized water at 60°C for one hour and then rinsed in deionized water and dried in a stream of nitrogen. The coupons were frequently still somewhat hydrophobic so the process was repeated (generally two times) until the coupons were completely hydrophilic. In the second case, coupons were immersed in a solution consisting of 5% nitric acid, 30% phosphoric acid, and 65% deionized water at room temperature for five minutes, rinsed in deionized water, and dried in nitrogen.

The surfaces of the coupons were then examined using scanning electron microscopy (SEM). Coupons that were cleaned using the alkaline cleaner had a few large etch pits on their surfaces but the surfaces of such coupons were generally quite smooth (see Figure 11). Coupons that were given the acid etching pretreatment had a much coarser surface structure with numerous small etch pits (see Figure 12).

Rough, porous surface structures such as that obtained by the acid etching pretreatment are generally considered to be favorable for the formation of strong, durable adhesive bonds. The pores on such surfaces can be penetrated by primers or adhesives, resulting in mechanical interlocking and very strong bonds between the adhesive and the substrate. When transformations in the oxide are inhibited, bonds with excellent hydrothermal stability can also be obtained. An outstanding example is provided by the oxide obtained by anodizing aluminum in phosphoric acid (8). In that case a rough, porous oxide is obtained which has a thin

film of $AlPO_4$ on the surface. The rough, porous film inhibits hydration of the oxide, providing outstanding durability (8).

We consider the acid etch described above to be a suitable pretreatment process for steel. The etching can be done quickly and at room temperature. The porous oxide obtained should enable strong bonds to be obtained to the steel substrate. Durability should be provided through the use of primers containing silane coupling agents. We will probably adopt this process for subsequent work on bonding neoprene to steel.

Silanes for Bonding Neoprene to Steel and Aluminum

We have considered the use of several silanes, including γ-aminopropyltriethoxysilane (γ-APS), γ-aminoethylaminopropyltrimethoxy-silane (γ-AEAPS), and γ-mercaptopropyltrimethoxysilane (γ-SPS), for bonding neoprene to metals such as steel and aluminum. Generally speaking, only γ-AEAPS showed sufficient reactivity with neoprene to warrant further investigation.

Thin slabs of neoprene were cured against steel coupons that had been pretreated with dilute aqueous solutions of silanes. The rubber was then peeled from the coupons and the effectiveness of the silanes as primers for improving the dry adhesion of neoprene to steel was evaluated in a qualitative fashion. The neoprene always peeled easily from coupons that were primed with γ-APS. Failure of such samples was apparently along the neoprene/γ-APS interface. Adhesion of neoprene to coupons that were primed with γ-SPS was somewhat better. The rubber could still be peeled from the coupons rather easily but in this case the failure was at least partially cohesive within the rubber. The most effective primers were obtained from films formed by γ-AEAPS deposited on the coupons from 2% aqueous solutions at pH 8.0 and then dried at 100°C for 10 minutes. It was very difficult to

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peel the rubber from coupons having such primers without tearing the rubber. Failure was always cohesive within the rubber.

The reasons for this behavior are probably related to the extent of reaction between the silane primers and the neoprene. The reaction between an aminosilane and neoprene probably proceeds as follows:

$$-CH_2-\overset{\displaystyle |}{\underset{\displaystyle |}{C}}-\ +\ RNH_2\ \rightarrow\ -CH_2-\overset{\displaystyle |}{\underset{\displaystyle |}{C}}-\ +\ HCl$$
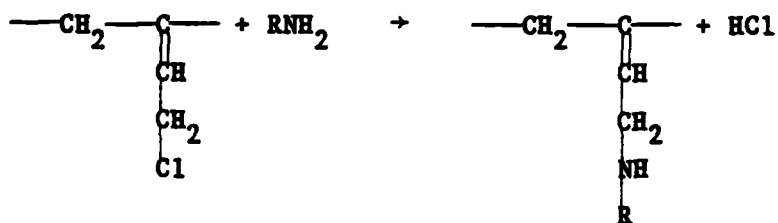
γ-AEAPS has more amino groups than γ-APS and is more reactive toward neoprene than γ-APS. The chlorine atom adjacent to the double bond in neoprene reduces the reactivity of the double bond, probably accounting for the limited reaction between mercaptosilane primers and neoprene that was observed.

Other results have indicated that γ-AEAPS also reacts with chlorinated rubbers of the "Parlon" type. It has been concluded that γ-AEAPS should be useful in formulating primers and adhesives for bonding neoprene to metals such as steel and aluminum.

Adhesive System for Bonding Neoprene to Steel

We have formulated a new primer system for bonding neoprene rubber to metals such as steel and aluminum. The development of this system has been guided by several principles. As indicated above, it is very difficult to obtain hydrothermally stable bonds between non-polar rubbery polymers such as neoprene and hydrophilic surfaces such as metal oxides without the use of a primer that can be crosslinked at the interface between the rubber and the oxide. Moreover, it is essential to inhibit moisture-induced transformations in the oxide.

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With these considerations in mind, we have prepared a new primer based on a crosslinkable epoxy resin and two silane coupling agents. The epoxy used was similar in structure to the diglycidyl ether of bisphenol-A. One of the silanes (phenyltrimethoxysilane) was chosen to provide some hydrophobic character to the primer, thereby reducing the amount of water reaching the surface of the oxide. The second silane (γ-aminoethylamino-propyltrimethoxysilane or γ-AEAPS) was chosen for its ability to crosslink the epoxy resin and to react with chlorinated rubbers and for its ability to adsorb onto metal oxides and inhibit moisture-related transformations within those oxides. We have also prepared a new adhesive based on a chlorinated rubber ("Parlon") for bonding neoprene rubber to the primer just described.

Results obtained so far indicated that the dry strength of adhesive bonds between neoprene and steel obtained using the new primer and adhesive is excellent and comparable to the dry strength of bonds obtained using the Chemlok 205/220 system. For example, neoprene rubber was cured against three steel coupons that had been pretreated in different ways and the rubber was then peeled from the steel. The failure surfaces are shown in Figure 13. When the rubber was cured against a coupon that had been acid etched and then pretreated with the new epoxy primer, strong bonds were obtained and it was very difficult to peel the rubber from the coupon. The locus of failure was near the steel surface but was clearly cohesive within the rubber (see Figure 13A). When neoprene was laminated against a coupon that had been etched and primed as before and then coated with a thin film of the new chlorinated rubber adhesive, it was essentially impossible to peel the rubber from the steel. In such cases the locus of failure was cohesive in the bulk of the rubber and large segments of the rubber

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remained on the substrate (see Figure 13B). When neoprene was laminated against a steel coupon that had been etched and primed as before and then coated with a thin film of Chemlok 220 adhesive, similar results were obtained (see Figure 13C).

Preliminary results indicate that the wet strength of adhesive bonds obtained using the new adhesive system is also promising. In one series of experiments, the new primer and adhesive were applied to steel coupons that had been acid etched. Neoprene was then laminated onto the coupons and the coupons were immersed in water at room temperature for four days. Qualitative testing indicated that there was no loss in bond strength and the locus of failure was still cohesive within the bulk of the rubber.

In another series of experiments, neoprene was laminated onto steel coupons that had been pretreated with the new primer and adhesive and the coupons were then immersed in boiling water for two hours. Qualitative peel testing indicated no significant loss in bond strength.

VI. FUTURE WORK

During the next phases of this research, we will use the new primer and adhesive to bond neoprene to steel and also to aluminum. Quantitative mechanical testing will be done to determine the strength and durability of neoprene/metal adhesive bonds during exposure to aggressive environments such as artificial sea water for long times and surface analysis techniques such as x-ray photoelectron spectroscopy (XPS) will be used to examine the failure surfaces and to determine the failure mechanisms. In all cases the results obtained using the new adhesive system will be compared to those obtained using the commercial Chemlok 205/220 system.

The performance of the new adhesive system will be optimized by adjusting its composition by, for example, varying the relative amounts of the two silanes in the primer. If necessary, the formulation of still other new adhesive systems will be considered. However, the principles discussed above will be adhered to. That is, any adhesive system for obtaining environmentally stable bonds between rubbery polymers and the oxidized surfaces of metals must include a primer that can be crosslinked at the metal oxide surface and can inhibit transformations within the oxide.

V. REFERENCES

1. Plueddemann, E. P., *Silane Coupling Agents*, Plenum Press (New York), 1982, p. 126.

2. Buchan, S., *Rubber to Metal Bonding*, Crosby Lockwood and Son (London), 1948.

3. Coleman, E. W. and D. M. Alstadt, U. S. Patent 2,900,292, August 18, 1959.

4. Erickson, P. W. and E. P. Plueddemann, in *Composite Materials*, vol. 6, L. J. Broutman and R. H. Krock, eds., Academic Press (New York), 1974, Ch. 1.

5. Ahagon, A., Gent, A. N., and E. C. Hsu, in *Adhesion Science and Technology*, vol. 9A, L. H. Lee, ed., Plenum Press (New York), 1975, p. 281.

6. Plueddemann, E. P., *Silane Coupling Agents*, Plenum Press (New York), 1982, , p. 162.

7. Trawinski, D. L., SAMPE Quarterly *16*, 1 (1984).

8. Davis, G. D., Sun, T. S., Ahearn, J. S., and J. D. Venables, J. Materials Sci. *17*, 1807 (1982).
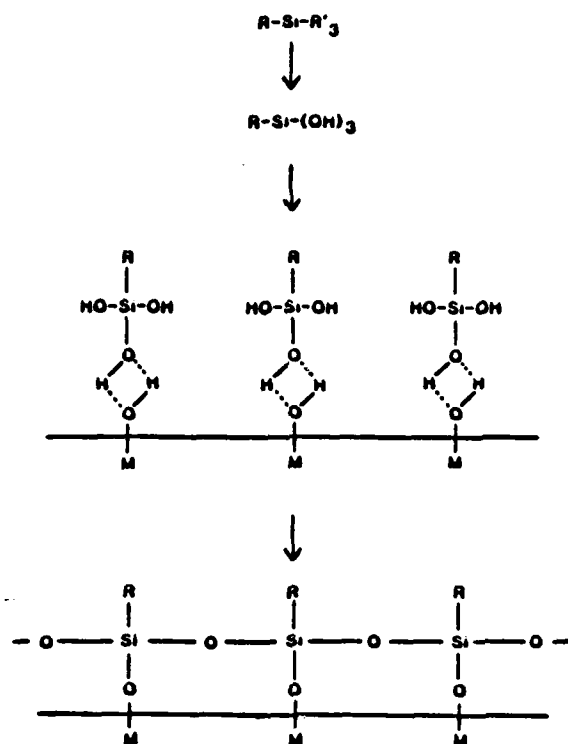
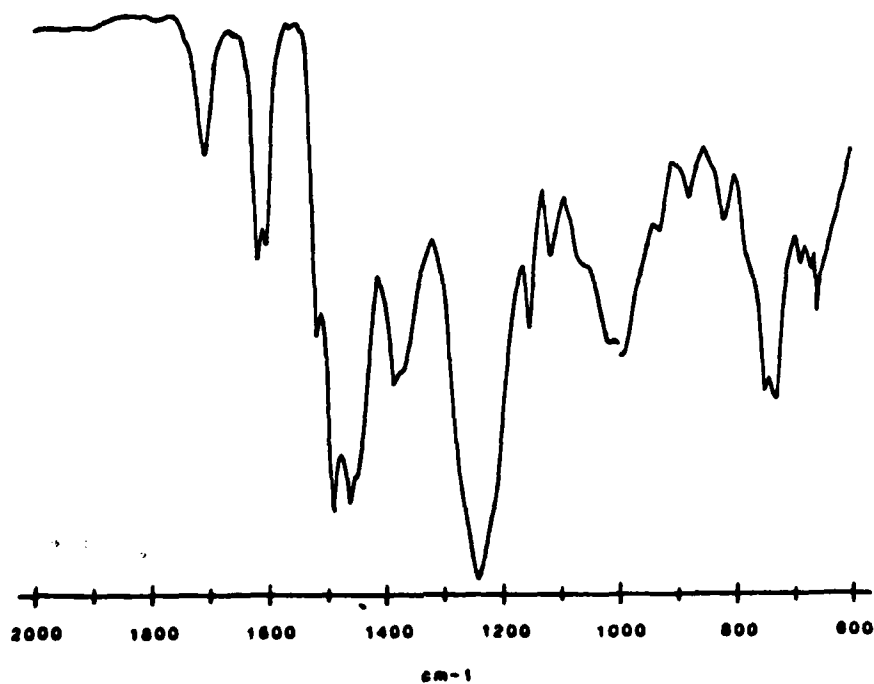Figure 1. Chemical bonding theory describing mechanism by which silane primers function.

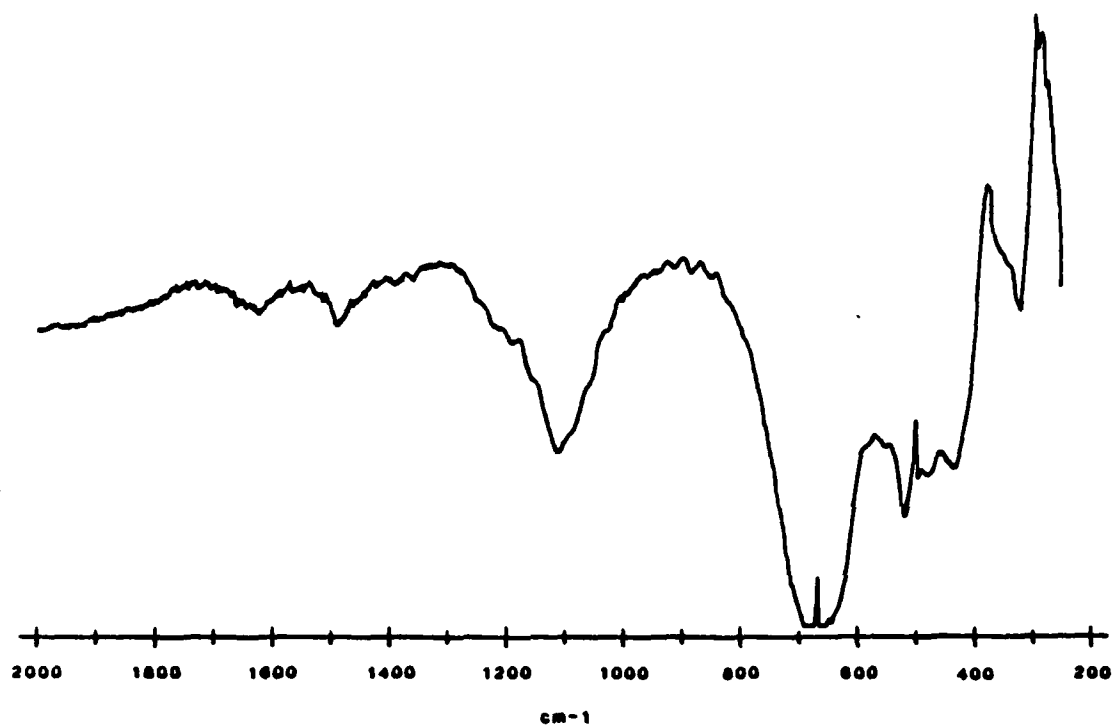Figure 2. Transmission infrared spectrum of polymer film obtained from Chemlok 205.

Figure 3.. Transmission infrared spectrum of solids separated from Chemlok 205.
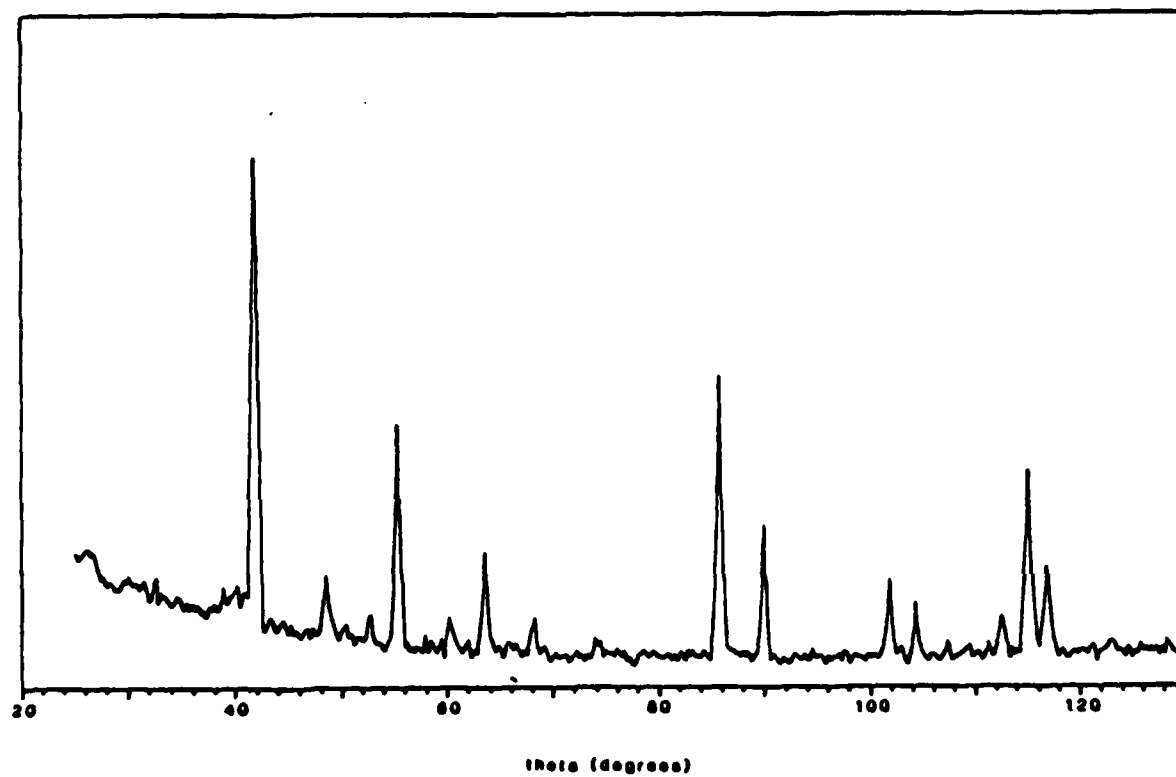

theta (degrees)

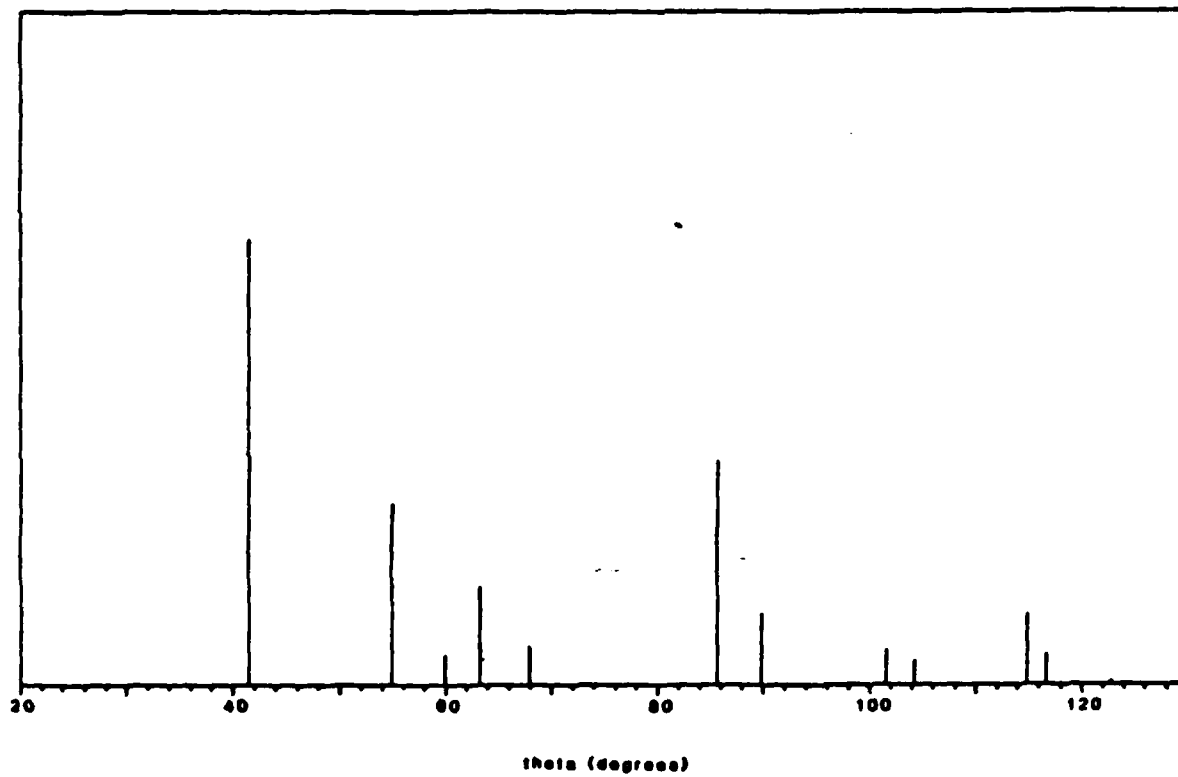Figure 4. X-ray scattering from solids separated from Chemlok 205.

Figure 5. Expected x-ray scattering from rutile TiO_2.

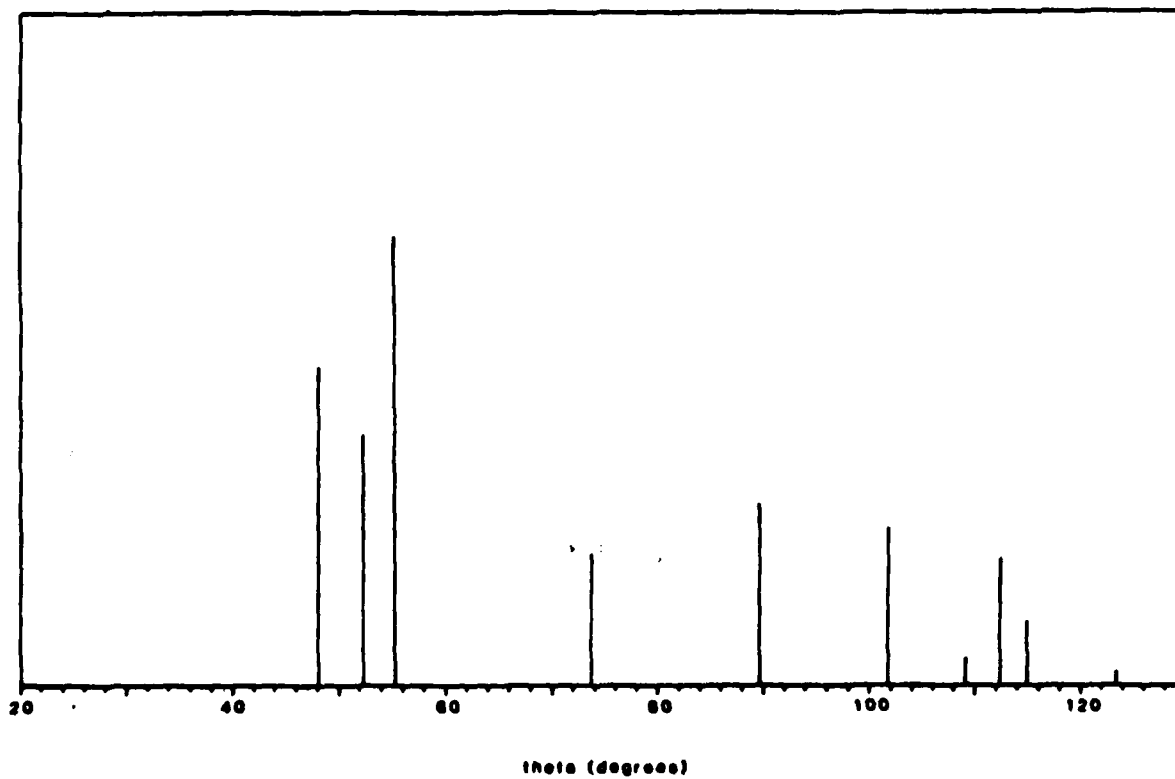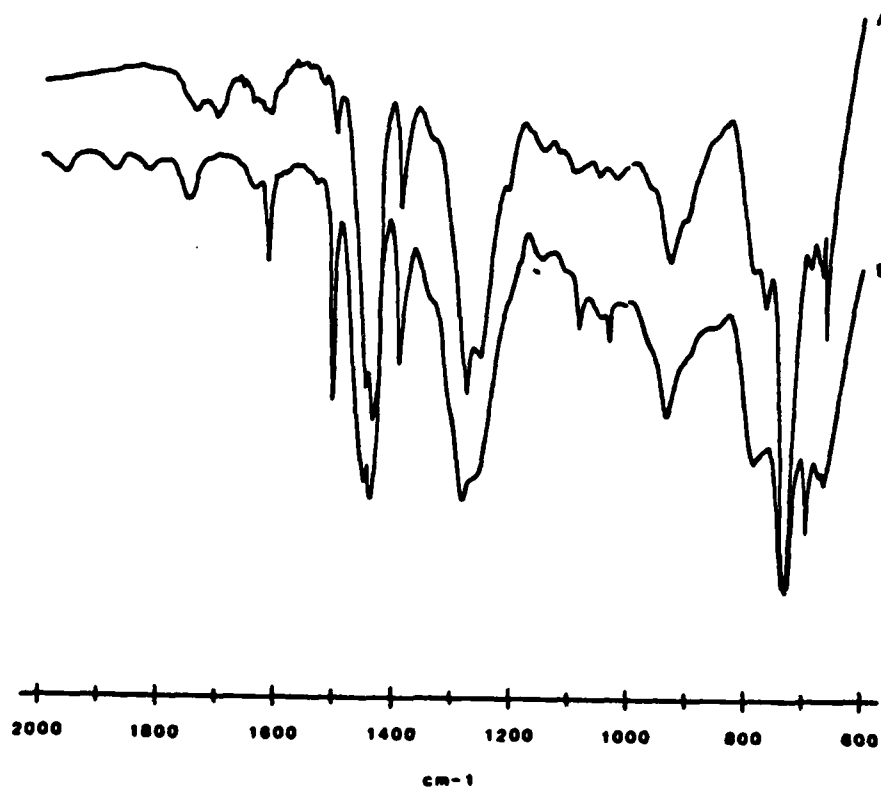Figure 6. Expected x-ray scattering from ZnO.

2000   1800   1600   1400   1200   1000   800   600

cm-1

Figure 7. Transmission infrared spectrum of (A) – Chemlok 220 cast film and (B) – Parlon S-10.

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BINDING ENERGY, eV
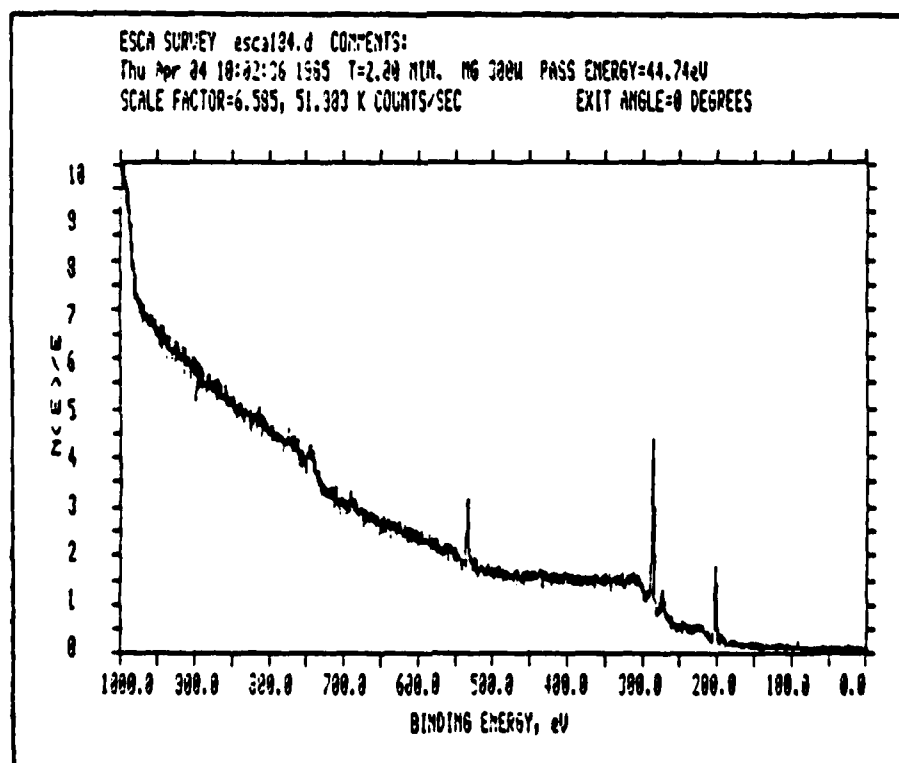
Figure 8. X-ray photoelectron survey spectrum of Chemlok 205 primer.

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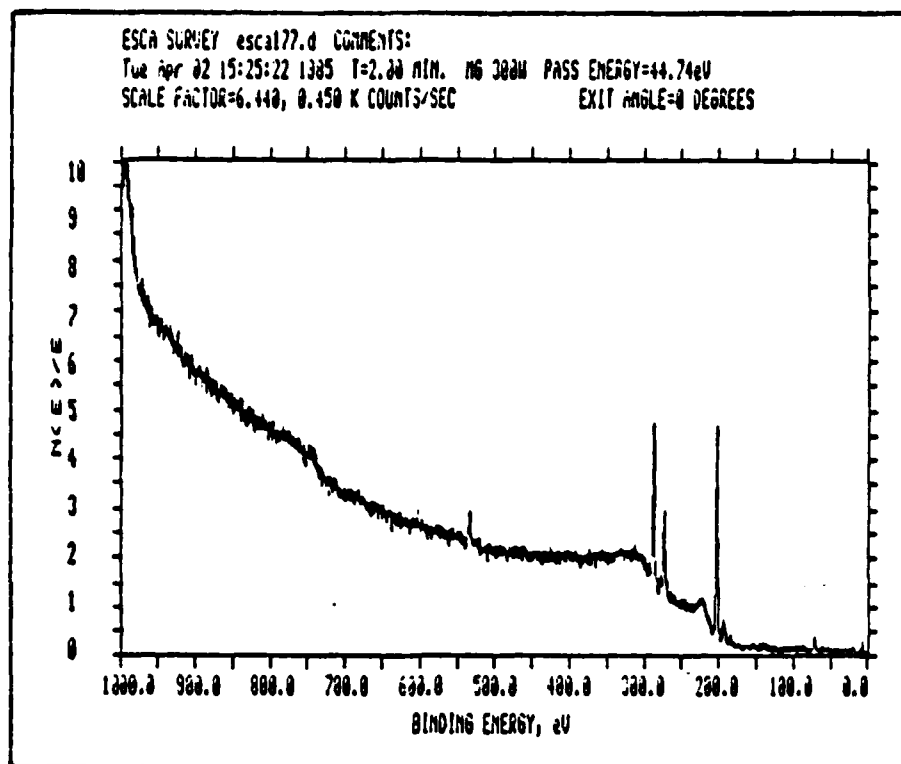
Figure 9.   X-ray photoelectron survey spectrum of Chemlok 220 adhesive.

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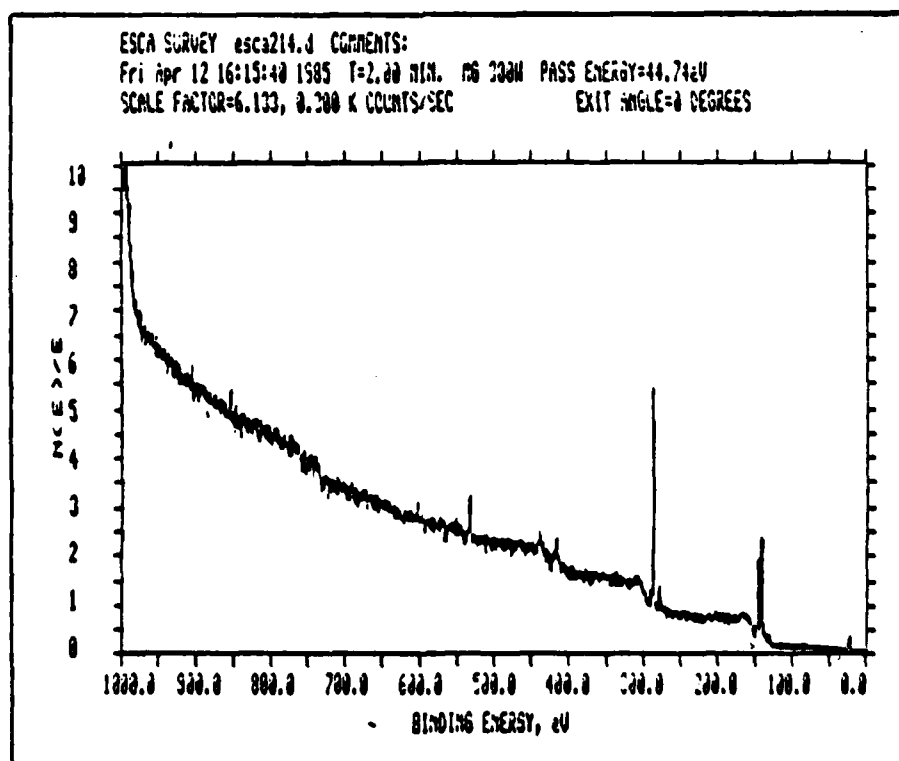SCALE FACTOR=6.133, 0.300 K COUNTS/SEC   EXIT ANGLE=0 DEGREES

Figure 10.   X-ray photoelectron survey spectrum of neoprene rubber.

Figure 11. Scanning electron micrograph of steel surface after
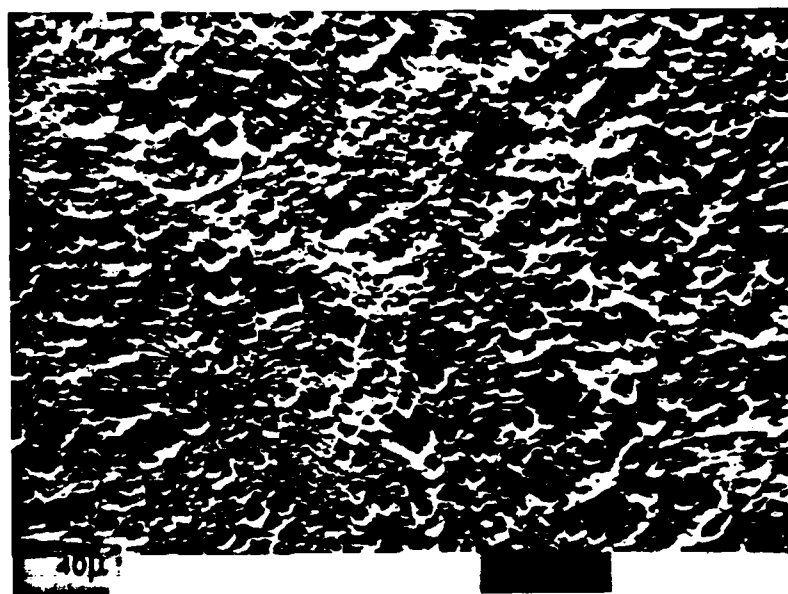cleaning in Parker 348 solution; 500X.

Figure 12. Scanning electron micrograph of steel surface after
acid etch; 500X.

Figure 13. Fracture surfaces of neoprene/steel adhe-
sive bonds. The substrate pretreatment
consisted of acid etching followed by
(A) - epoxy primer, (B) - epoxy primer and
chlorinated rubber adhesive, and (C) - epoxy
primer and Chemlok 220 adhesive.

VI. PUBLICATIONS AND PRESENTATIONS

The following is a summary of publications and papers presented at technical meetings during the preceding year based on work supported by this contract:

"Laser-Excited Raman Spectroscopy," presented at Vibrational Spectroscopy of Polymers and Energy Related Materials, short course sponsored by Case Western Reserve University, Cleveland, Ohio, August 20-24, 1984.

"Reflection-Absorption Technique," presented at Vibrational Spectroscopy of Polymers and Energy Related Materials, short course sponsored by Case Western Reserve University, Cleveland, Ohio, August 20-24, 1984.

"Coatings and Adhesives on Metals," presented at Vibrational Spectroscopy of Polymers and Energy Related Materials, short course sponsored by Case Western Reserve University, Cleveland, Ohio, August 20-24, 1984.

"Structure and Properties of Silane Primers for Adhesive Bonding of Iron, Titanium, and Aluminum," presented at Adhesion Principles and Practice for Coating and Polymer Scientists, short course sponsored by Kent State University, Kent, Ohio, May 21-25, 1984.

"Silane Primers for Improved Hydrothermal Stability of Adhesive Bonds," presented at Virginia Tech Center for Adhesion Science Program Review/Workshop, Blacksburg, Virginia, April 29-May 2, 1984.

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